3-Hydroxy-3-methylglutaric Acid (V). At room temperature, 0.1 g of sodium nitrite was added to 20 ml of 50% nitric acid (d 1.31), and this was followed at 35-40°C by 5.2 g (0.04 mole) of mevalonolactone (IV) and the reaction mixture was stirred at the same temperature for 5 h. The bulk of the nitric acid was distilled off, water (2 × 50 ml) was added to the residue, and the water was distilled off from the reaction mixture completely. The residue was dried in the air and, after recrystallization from acetone, 4.8 g (76%) of the acid (V) was obtained with mp 110°C [6].

LITERATURE CITED

1. O. Hiroaki, M. Huroshi, M. Tetsuo, and S. Shojiro, *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, No. 7, 1021 (1971).
2. O. Hiroaki, M. Tetsuo, and S. Shojiro, *J. Synth. Org. Chem. Jpn.* **36**, No. 10 (1978).
3. B. Asoke and K. Govind, *Synth. Commun.* **12**, No. 3, 225 (1982).
4. J. E. Dubolset and C. Moulineau, *Bull. Soc. Chim. Fr.*, 1134 (1967).
5. S. K. Ogorodnikov and G. S. Idlin, *The Production of Isoprene* [in Russian], Khimiya, Leningrad (1973), p. 25.
6. R. Tscheshe and H. Machleidt, *Ann. Chem.* **631**, 61 (1960).

STRUCTURE OF PORPHYRINS OF KARAZHANBASS PETROLEUM

R. N. Nasirov

UDC 543.42;547.741;553.982

The spectral type and structure of the porphyrins isolated from Karazhanbass petroleum have been studied with the aid of electron spectroscopy in combination with the PMR method.

The wide use of porphyrins and metalloporphyrins as medicinal preparations, semiconductors, and sensitizers and the creation from porphyrins of catalysts for chemical and enzymatic processes, and also the synthesis of expensive derivatives of them, explain the great interest in investigations of petroleum porphyrins [1, 2]. In the present paper we consider the composition and structure of the porphyrins of the Karazhanbass petroleum with high levels of the vanadyl complex (230 mg/100 g of petroleum) and of the nickel complex (23.9 mg/100 g of petroleum) of the porphyrins, which have been studied by the methods of electron spectroscopy, electron spin resonance (ESR), and proton magnetic resonance (PMR).

Metalloporphyrin concentrates were isolated by extraction with acetone. The vanadyl and nickel porphyrins of the Karazhanbass petroleum were separated by the procedure of [3] with the aid of absorption column chromatography on silica gel. The nickel porphyrins were eluted with hexane—benzene (1:1) and the vanadyl porphyrins with chloroform. To identify the nickel and vanadyl porphyrins and to determine their ratio we used the results of their electronic absorption spectra in the visible region (Fig. 1). The total amount of vanadyl complexes was checked by the ESR method [14].

Baker et al. [5] have proposed to use the ratio of intensities α/β of the bands of the nickel complexes (Fig. 1b) to evaluate the relative amount of deoxophylloerythroetioporphyrin (DPEP) and etioporphyrin (EP) in a mixture. In the case of the complex that we are studying, this ratio is 3.0, showing that in petroleum nickel porphyrin is present in the form of the etio type.

It is known that the magnitude α/β can also be used for a preliminary characterization of the composition of vanadyl complexes of geoporphyrins if their spectral types are known; however, as will be shown below, to estimate the comparative amounts of DPEP and EP the use of the ratio α/β for the preliminary characterization of the vanadyl complexes of porphyrins has proved to be unsuitable because of their mutual superposition ($\alpha/\beta = 1.75$) (Fig. 1a).

A more commonly used method of determining spectral types is an analysis of the electronic spectra of the demetallated porphyrins. To prepare them for investigation, a benzene solution of vanadyl porphyrins was subjected to demetallation with concentrated sulphuric acid as in [3]. After purification, the free porphyrins with different structures were separated with the aid of column chromatography on silica gel LS 5/40. Benzene was used as the eluent. The porphyrins of the etio series were eluted first and were followed by the DPEP.

Institute of the Chemistry of Petroleum and Natural Salts, Academy of Sciences of the Kazakh SSR, Gur'ev. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 32-35, January-February, 1990. Original article submitted December 7, 1988; revision submitted August 8, 1989.

0009-3130/90/2601-0025$12.50 ©1990 Plenum Publishing Corporation

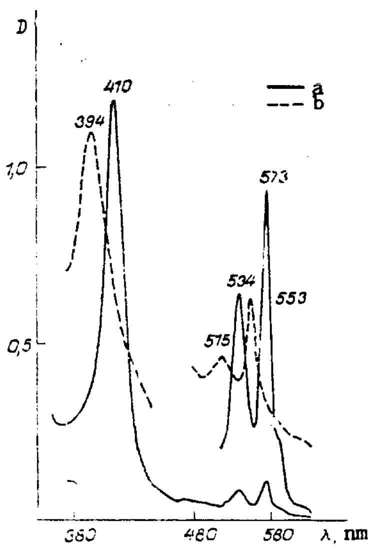

Fig. 1. Absorption spectra in the visible region in chloroform of the vanadyl (a) and nickel (b) porphyrin complexes isolated from the petroleum of the Karazhanbass deposit (bore hole 105).

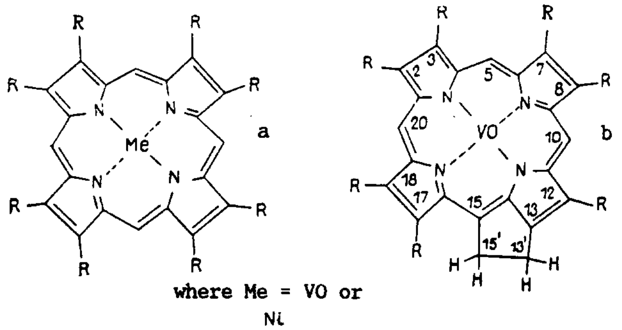

Fig. 2. Structures of the porphyrins isolated from the Karazhanbass petroleum: a) etio type; b) DPEP; R) an alkyl substituent.

Analysis of the electronic absorption spectra in the visible region of the free bases showed the presence of two main series — DPEP and EP, differing by the intensity of their absorption bands. The spectrum of DPEP, containing an isocyclic ring, with λ_{max} 502, 536, 565, and 620 nm, was characterized by the relationship of the intensities IV > I > II > III. In the case of the etio type four absorption bands were observed in the visible region at 498, 533, 565, and 620 nm with intensities in the relationship IV > III > II > I.

The relative amounts of EP and DPEP in the petroleum studied were determined with the aid of the additivity rule [6] and from the intensity of the Soret band (398 nm): 60 and 40%, respectively.

The results obtained confirmed that in the mass of the vanadyl porphyrins the main structural group consists of alkyl porphyrins and DPEP (Fig. 2), which agrees well with the results of an analysis of the Karazhanbass petroleum by mass spectrometry [7, 8].

To obtain more detailed information on the structures of the spectral types of porphyrins, the porphyrins isolated were studied by the proton magnetic resonance (PMR) method. In the PMR spectrum of a porphyrin containing a cyclopentane ring, unresolved multiplets of the 15'-CH_2 group are observed in the 5.20-ppm region. The signal from a 13'-CH_2 group is observed in the 4.21-ppm region. The protons of the three meso positions (5-, 10-, and 20-H) are represented by signals at 10 ppm. The signals of protons in the pyrrole substituted $-CH_3$ and $-CH_2-$ appear in the form of multiplets in the 3.55- and 4.10-ppm regions, respectively. Signals from the CH_3 group of an ethyl substituent are observed at 1.80 ppm. The NH signal appears at 4.7 ppm. The PMR spectrum of the DPEP from the Karazhanbass petroleum was similar to the PMR spectrum of the DPEP from the West Surgut deposit [9].

The results obtained confirm that in the petroleum studied there was a considerable amount of DPEP, which is formed, according to Treibs' scheme [10], from α-chlorophyll on the reduction of the 3-vinyl and 13'-carbonyl substituents with dehydrogenation of the chlorine system to a porphyrin system by the hydrolysis of ester groups and decarboxylation. The scheme also includes the elimination of magnesium and conversion into a complex of porphyrin with vanadium. The transition from the DPEP series to the etio series takes place through the opening of the isocyclic ring in an acid medium.

For the nickel porphyrins, the appearance of compounds of the etio series apparently takes place under milder conditions than in the case of the vanadyl complexes, which explains the dominating role of Ni-EP as compared with Ni-DPEP.

EXPERIMENTAL

The electronic absorption spectra of the vanadyl and nickel porphyrins, and also the spectra of the free porphyrins, were taken on a Specord UV-Vis spectrophotometer at room temperature.

The ratio of the vanadyl porphyrins to the nickel porphyrins was determined spectrophotometrically. The level of vanadyl porphyrins (mg/100 g of petroleum) was determined directly by the method of electron spin resonance (ESR) on a modernized RÉ-1301 radiospectrometer with an automated temperature attachment at −90°C. Martyshinskaya petroleum (bore hole 132) with a known vanadyl porphyrin content (0.32 mg/100 g) was used as concentration standard.

The PMR spectra of the porphyrins isolated were obtained on a Bruker WP-200 SY spectrometer with a working frequency of 200 MHz in deuterochloroform solution with TMS as internal standard.

LITERATURE CITED

1. K. A. Askarov, B. D. Berezin, R. P. Evstigneeva, et al., *The Porphyrins, Structure, Properties, Synthesis* [in Russian], Vol. 1, Nauka, Moscow (1985).
2. Abstracts of Lectures at the 5th All-Union Conference on the Coordination and Physical Chemistry of the Porphyrins, Ivanovo (1988).
3. O. V. Serebrennikova and T. V. Belokon , *The Geochemistry of the Porphyrins* [in Russian], Nauka, Novosibirsk (1984).
4. R. N. Nasirov, S. P. Solodovnikov, and B. U. Urazgaliev, *Khim. Tekhnol. Topliv. Masel*, No. 1, 56 (1978).
5. E. W. Baker, S. E. Palmer, and W. Y. Huang, "Intermediate and late diagenetic tetrapyrrole pigments," *Leg 41: Cape Verde Rise and Basin*: Initial Report of the Deep Sea Drilling Project, Vol. 41 (1978), p. 825.
6. V. R. Antipenko, V. N. Plugar , S. L. Gusinskaya, and V. I. Titov, *Neftekhimiya* **16**, No. 4, 620 (1976).
7. S. F. Bakirova, A. V. Kotova, S. Yag'yaeva, N. V. Fedorova, and N. K. Nadirov, *Neftekhimiya* **24**, No. 6, 783 (1984).
8. A. V. Kotova, S. F. Bakirova, S. M. Yag'yaeva, and I. D. Leonov, *Geokhimiya*, 1644 (1986).
9. T. K. Mozzhelina, O. V. Serebrennikova, A. M. Shul'ga, and V. I. Titov, *Neftekhimiya* **23**, No. 4, 562 (1983).
10. A. Treibs, "Chlorophyll- und Häminderivate in Organischen Mineralstoffen," *Angew Chem.* **49**, 582 (1936).